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13. ABSTRACT *(Maximum 200 words)*

This grant studies the band gap bowing and miscibility in wide-band-gap nitride alloy systems by means of first principles LMTO calculations. Calculations were completed for $Al_xB_{1-x}N$ and $In_xGa_{1-x}N$ ordered structures and disordered alloys using a cluster expansion approach. Bond-length relaxation effects on the energy of formation were investigated using a Keating model for $Al_xB_{1-x}N$. Their effects on the band-gap bowing were investigated for $In_xGa_{1-x}N$. Band structure calculations were completed for GaP as a function of lattice constant. A virtual crystal approach was tested for $In_xGa_{1-x}N$ and for $(SiC)_{1-x}(AlN)_x$ and found to underestimate bowing in both cases.

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Modelling of Wide-Band-Gap Semiconductor Alloys

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1 Grant history

The original period for this research grant was Aug. 1, 1994 to July 31, 1995 and was for a total amount of $35,000. A renewal proposal was submitted in Janurary 1995 and approved. The requested amount for the renewal is $50,050. The renewal proposal contained the First Semiannual Progress Report for the first half of the grant period. The present document is the Second Semiannual Progress Report. Related to this grant, an AASERT grant (N00014-95-1-0959) entitled "Growth and characterization of $Al_{1-x}B_xN$ Alloys," was awarded March 15, 1995 for a total amount of $135,520 for a period of 3 years.

2 Research Goals

The research goals of this project are to model the miscibility, band-gap bowing, and related properties of wide-band-gap nitride alloys and related materials by means of first-principles electronic structure calculations.

3 Technical description of progress

3.1 $Al_xB_{1-x}N$

The first alloy sytem we chose to investigate is the $Al_xB_{1-x}N$ system. This system is characterized by a large lattice-mismatch (20 %) and its prospects for synthesis are still rather uncertain. Its growth is the subject of the AASERT grant associated with the present grant. The first successful growth of mixed Aluminum Boron Nitride films was recently reported by Edgar *et al.* [1].

Electronic structure calculations were completed for the five Connoly-Williams ordered structures and subsequently used as a basis for modelling the disordered alloys by means of the cluster expansion technique. These calculations were for the idealized structural models without bond length relaxation. As expected, the formation energy was found to be high. Band-gap bowing was found to be substantial. The bond-length relaxation effects on the energy of formation were estximated using the semi-empirical Keating

model. This work was accomplished during the first half year and has been reported on in the renewal proposal. See the latter for further details.

3.2 $In_xGa_{1-x}N$

The second alloy system we investigated was $In_xGa_{1-x}N$. The lattice mismatch in this system is substantial (10 %) but less than in the $Al_{1-x}B_xN$ case (20 %). Again, we used the Connolly-Williams structures and cluster expanion method. Bond lenth relaxation was carried out using the Keating model. The Keating model parameters were extracted from our recent full-potential LMTO calculations of the elastic constants combined with experimental information on the LO-TO phonon splitting. The latter is related to the long-range Coulomb effects and gives a good measure of the effective charges. The effects of the bond lenth relaxation on band-gap bowing were calculated and found to be substantial.

In addition, we investigated the possibility to use the simpler virtual-crystal approximation (VCA) for this system. Our particular implementation of the VCA consists in averaging the LMTO (linear muffin-tin orbital) potential parameters in proportion to the concentration of the constituents. Within this approach each cation or anion is assumed to exhibit an average behavior of those in the two parent semiconductors. Fluctuations around this average are not included. We studied two slightly different levels of this approximation. In the first case, the parameters are used directly as obtained by the averaging procedure. In the second approach, we allowed for a charge re-arrangement between cation and anion, which leads to constant shifts of their respective potentials. We found that the difference between these two procedures to be small. The VCA was found to lead to reasonable results for the band gap bowing in this system, although it somewhat underestimates it. In particular, the bond-length relaxation effect on the band gap bowing which is substantial, is obviously not included in this approach. We find the band gap bowing in this system to be quite small in the absence of bond length relaxations. In other words, the band gap behaves nearly linearly with concentration. This was previously found to be the case also in $Al_xGa_{1-x}N$ [2]. The difference with the latter system is that it is much closer lattice matched and hence the final band-gap bowing including relaxation effects stays very small. We emphasize though that a-priori, it is not at all evident why the band-gap bowing in the absence of relaxations should be small. In

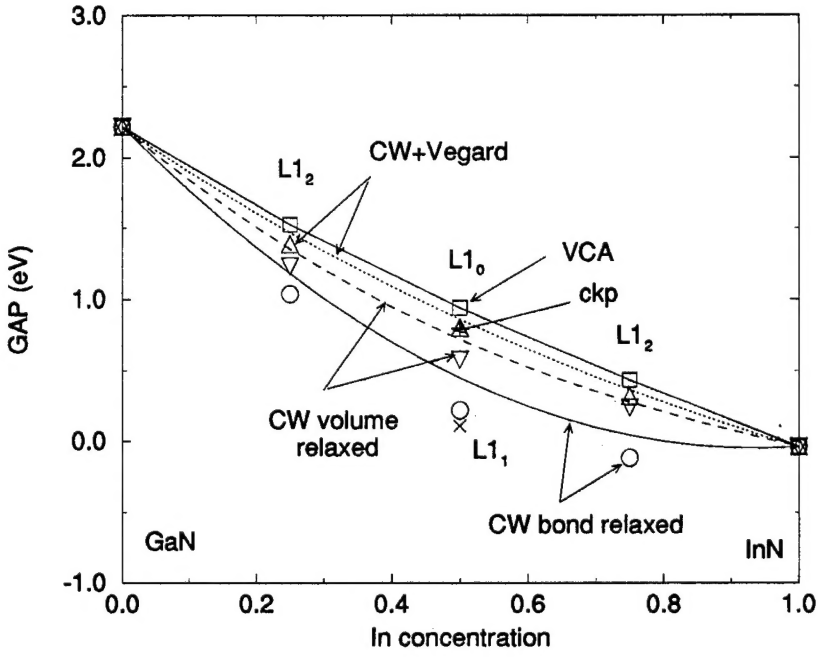

Figure 1: Band-gap bowing in $In_xGa_{1-x}N$ alloys in various approximations. The squares and full line indicate the band gaps within the VCA. The upward triangles indicate the band gaps of the ordered Connolly-Williams (CW) structures at the appropriately averaged lattice constant (according to Vegard's rule) and in the ideal structure. The dotted line gives the corresponding band gap behavior in the disordered alloys using the cluster expansion method. The downward pointing triangles and dashed line give the corresponding results for the volume relaxed case but still using the ideal structure. The circles and lower full line give the results including bond length relaxation. Some addition structures at 50 % concentration (chalcopyrite and $L1_1$ ordering) are indicated by a + and $\times$ symbol.

fact, this is not always the case.

Fig. 1 gives an overview of our band-gap bowing results for $In_xGa_{1-x}N$. We note that all the gaps in this figure are the LDA gaps which are an underestimate of the true quasiparticle gaps by about 1 eV in GaN and almost 2 eV in InN. We note that this correction can be linearly interpolated and hence does not influence the band gap bowing. One may see that the bandgap bowing is positive (i.e. sublinear) and is increasing as our model becomes more sophisticated and includes the physical complexity of the system more fully. We also note the anomalously low bandgap of the $L1_1$ structure, which has been observed in other semiconductor alloy systems. The chalcopyrite structure may be seen to provide a good approximation for the disordered alloy behavior. (No relaxation of the chalcopyrite (CKP) structure was included sofar., Thus, it should be compared with the dotted and dashed line predictions.) This observation is in agreement with the fact that the CKP is one of the so-called special quasi random systems (SQS) which have as statistical property that they well reperesent the completely disordered system in their correlation functions.

3.3 $(SiC)_{1-x}(AlN)_x$

We reconsidered another alloy system, $(SiC)_{1-x}(AlN)_x$ we have previously investigated [3, 4] in the light of the virtual crystal approximation (VCA). In that particular case, since the cations (Si and Al) and anions (C and N) are neighboring atomic number (Z) elements of each other, it is possible to use an average atomic number approximation, which we named "virtual Z approximation" (VZA). It allows to perform fully self-consistent calculations for these hypothetical Z compounds. Our hope was that if this procedure works, it would provide a simple means to study the polytype dependence of in this alloy sytem. As is well known SiC can be found in a large number of crystal structures called polytypes which differ from each other in their one dimensional stacking of layers. A similar situation may occur for the corresponding $(SiC)_{1-x}(AlN)_x$ alloys for small x. For the other end of the concentration, i.e. close to pure AlN, the wurtzite structure appears to prevail.

Unfortunately, our calculations showed that within this VZA, the bandgap of $(SiC)_{1-x}(AlN)_x$ alloys varied nearly linearly, in sharp contrast with the behavior obtained in our previous work which showed a very large band gap

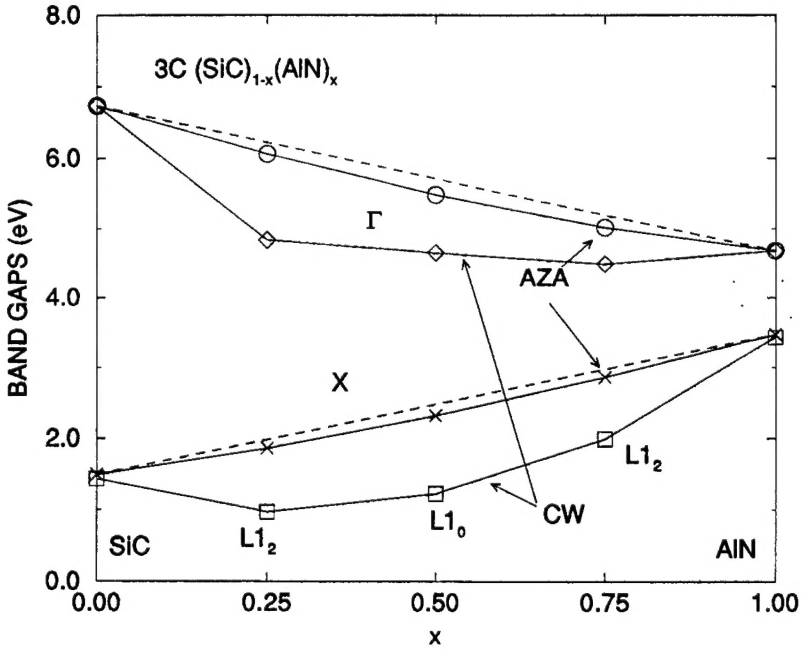

Figure 2: Band gap bowing in $(SiC)_{1-x}(AlN)_x$ alloys in the VZA and CW approximations. The dashed lines indicate the linear behavior. The lines marked with circles and $\times$ show the VZA behavior for the direct gap at Γ and indirect gap ($\Gamma - X$). The diamonds and squares provide the corresponding gaps in the CW ordered structures.

bowing in this system. In spite of this negative result, we believe that these results are quite instructive and provide new insights into the origins of band-gap bowing in this system. Further analysis is in progress.

Fig. 2 compares the results of the VZA and CW approaches for zincblende (or 3C) $(SiC)_{1-x}(AlN)_x$.

3.4 GaN_xP_{1-x}

The final system we started work on is the GaN_xP_{1-x} alloys sytem. The distinction form the previous nitride systems considered is that here we vary the anion instead of the cation. Large lattice mismatch (about 18 %) is present in this system. Our primarly motivation for the study of this system is that it has promise to adjust the band gap of GaN towards the low side so as to obtain pure blue light band-gap emission. (Current blue light emission from GaN LEDs is related to a transition involving the acceptor level and is less likely to lead to sufficient sharpness and intensity for laser operation.) It is an alternative system to In_xGa_{1-x} from this point of view and may suffer less from the difficulties inherent in working with InN. Although the mutual solubility of GaN and GaP was found to be very low, and was, in fact, used to grow GaN out of molten GaP with N doping by Grezegory et al.[5], the behavior near the other end of the concentration range close to GaN is not known. Furthermore, non-equilibrium epitaxial growth techniques may lead to different conclusions about the feasibility of such mixed films than the previous work on bulk systems.

As a starting point, we investigated pure GaP. In agreement with previous work, we found GaP to be an indirect gap semiconductor. Furthermore, however, we found that several conduction-band minima are quite close and may easily become inverted with lattice constant variation. In particular, this is important when we consider GaP at high compressions relevant to e.g. a 50 % alloy with GaN because according to Vegard's law, we then need to consider a 9 % compression.

4 Human resource development

One undergraduate student (Bill Dimmock) contributed to the study of GaP in partial fulfillment of a course "Research Experience".

One graduate student Kwiseon Kim is involved in the work on nitride elastic properties and alloys.

5 Dissemination of Results

Our preliminary results on the alloy systems considered here will be incorporated in some conference papers scheduled for Fall 95.

- "Electronic Properties of the Group III-Nitrides and their Alloys," W. R. L. Lambrecht, K. Kim and B. Segall, abstract accepted for the *Topical Workshop on III-V Nitrides*, Nagoya , September 1995.
- "Electronic and Optical Properties of the Group-III Nitrides, their Heterostructures and Alloys," Walter R. L. Lambrecht, Kwiseon Kim and Benjamin Segall, invited paper at the *First International Symposium on GaN and Related Materials*, Symposium AAA at the MRS Fall Meeting, Boston, Nov. 1995.

A paper in preparation for *Phys. Rev. B* on "Elastic constants and related properties of tetrahedrally bonded BN, AlN, GaN and InN," by Kwiseon Kim, Walter R. L. Lambrecht and B. Segall will contain our results on the derivation of Keating parameters for these materials.

Separate papers and/or and overview paper on the various alloys are planned for later when a more complete set of results are available.

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